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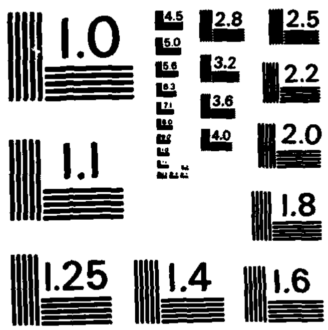

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ASSOCIATION OF POLYPHOSPHAZENES IN SOLUTION

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Intrinsic viscosity data on poly[bis(trifluoroethoxy)phosphazene] (PBFP) in acetone exhibited negative slopes in Huggin's-Kraemer's plots. Solutions of PBFP at concentrations of 0.3, 0.4, 0.6 and 0.8 g/100 ml were examined in transmission with an FTIR spectrometer. The increase in absorptivity of the solutions was much less than proportional to the increase in polymer concentrati[on] indicating that the calculated extinction coefficient decreased as the polymer concentration increased, implying polymer association in solution.

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ABSTRACT

Intrinsic viscosity data on poly[bis(trifluoroethoxy)phosphazene] (PBFP) in acetone exhibited negative slopes in Huggin's - Kraemer's plots. Solutions of PBFP at concentrations of 0.3, 0.4, 0.6 and 0.8 g/100 ml were examined in transmission with an FTIR spectrometer. The increase in absorptivity of the solutions was much less than proportional to the increase in polymer concentration, indicating that the calculated extinction coefficient decreased as the polymer concentration increased, implying polymer association in solution.

Association of Polyphosphazenes in Solution

Since the synthesis of linear stable polyphosphazenes in 1965 by Allcock et al[1] these polymers have received much attention. Still, some aspects of polyphosphazene research are controversal because of their unusual behavior. For instance, dilute solution viscosity analysed by the Huggins[2] and Kraemer[3] equations do not exhibit[4-6] the anticipated (theoretical) difference of 0.5 between the Huggin's constant (k') and the Kraemer constant (k"). Mention has been made of this discrepancy by Hagnauer and Schneider[4] when working with poly(fluoroalkoxyphosphazenes) using freon-ether as a solvent. Non-linear Huggins-Kraemer plots with negative slopes were reported and the anomalous behavior was attributed to the presence of adventitious polar groups such as P-OH, P-Cl P-NH- on the main polymer backbone. It was stated that relatively small amounts of acetone (9.09% V/V) inhibited or at least diminished this anomalous behavior.

Other workers[6] have performed intrinsic viscosity, osmotic pressure and light scattering measurements on aryloxy type phosphosphazenes. Based upon their light scattering measurements they remarked that they were unable to rule out the possibility that their polymers may exist in some kind of supermolecular structure in solution.

Since our intrinsic viscosity measurements of poly(bistrifluoroethoxyphosphazene), PBFP, in acetone exhibited Huggins-Kraemer plots with negative slopes at all polymer concentrations, an attempt was made to monitor changes in polymer aggregation in solution by infrared spectroscopy using a Digilab FTIR instrument. The spectra of PBFP polymers in acetone at concentrations ranging from 0.3 to 0.8 g/100 ml. in sodium chloride cells were examined in the transmission mode. Difference spectra between the polymer solution and the acetone was obtained

for each solution in the spectral window between 800 and 1100 cm^{-1} which was selected after the overall spectrum of PBFP, mixed and pelletized with KBr, was recorded in transmission, using a Beckmann IR9 spectrometer. This transmittance curve (400-4000 cm^{-1}) is illustrated in Figure 1 and the solution data are displayed in Figure 2. Particular attention is focussed upon the 965 cm^{-1} band of the $P-O-CH_2-CF_3$ group since anomalous intensity changes in this region should directly reflect aggregation behavior.

The molar extinction coefficient, ε, characteristic of the polymer in solution is plotted as a function of polymer concentration in Figure 3. This plot reveals that ε is strongly dependent upon concentration so that the Beer-Lambert law

$$A = -\log T = \varepsilon C\ell$$

is not obeyed. In this equation A and T are absorbance and transmission parameters, ε is the extinction coefficient, C is the concentration of solution and ℓ is the is the path length.

Association of the type: $n(A) \rightleftharpoons (A)n$ occurs since ε is not independent of concentration, but actually decreases as the polymer concentration in acetone increases, Since trifluoroethoxy groups are polar both inter-and intra- molecular interaction must be present.

Acknowledgement

Work supported in part by the Office of Naval Research; Contract #ONR 356-644. The authors also thank Professor D. M. Hercules for F.T.I.R. facilities.

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Figure Legends

Figure 1. Infrared spectra of PBFP in the transmission mode. The principal peak assignments are

1. $P-OCH_2CF_3$ ( )
2. $P-OCH_2CF_3$
3. P-N
4. $P-OCH_2CF_3$ ( )

Figure 2. FTIR transmission spectra of solutions of PBFP in acetone. Solution concentrations are:

A. 0.03 g/dl

B. 0.04 g/dl

C. 0.06 g/dl

D. 0.08 g/dl

Figure 3. Molar extinction coefficient, ε ,(arbitrary units) versus concentration for PBFP in acetone.

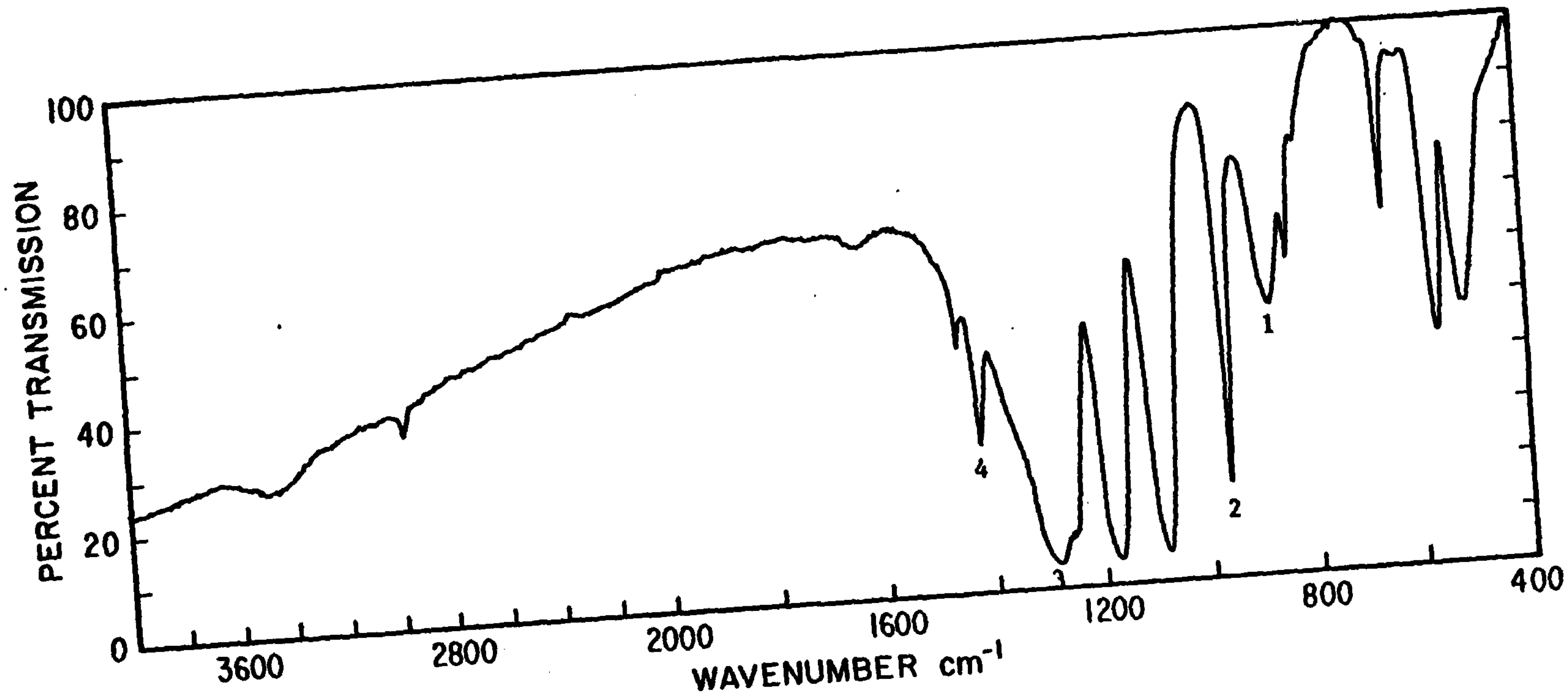

Figure 1 . Infrared Spectra of PBFP in Transmittance Mode. The Principal Peak Assignments are 1)P-OCH_2CF_3 2)P-OCH_2CF_3 3)P-N and 4)P-OCH_2CF_3.

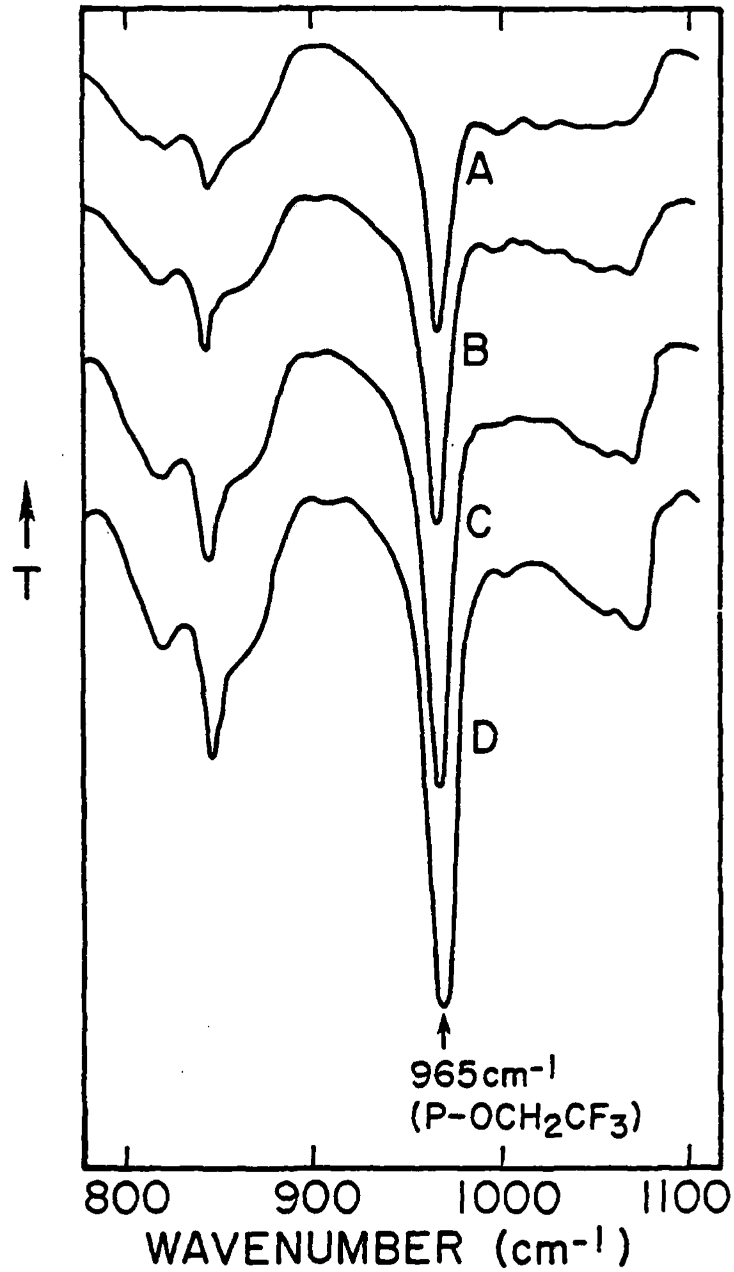

Figure 2 . FTIR spectra of solutions of PBFP in acetone, (transmission mode).A,solution concentration = 0.03 g/dl; B:0.04 g/dl; C:0.06 g/dl and D:0.08 g/dl.

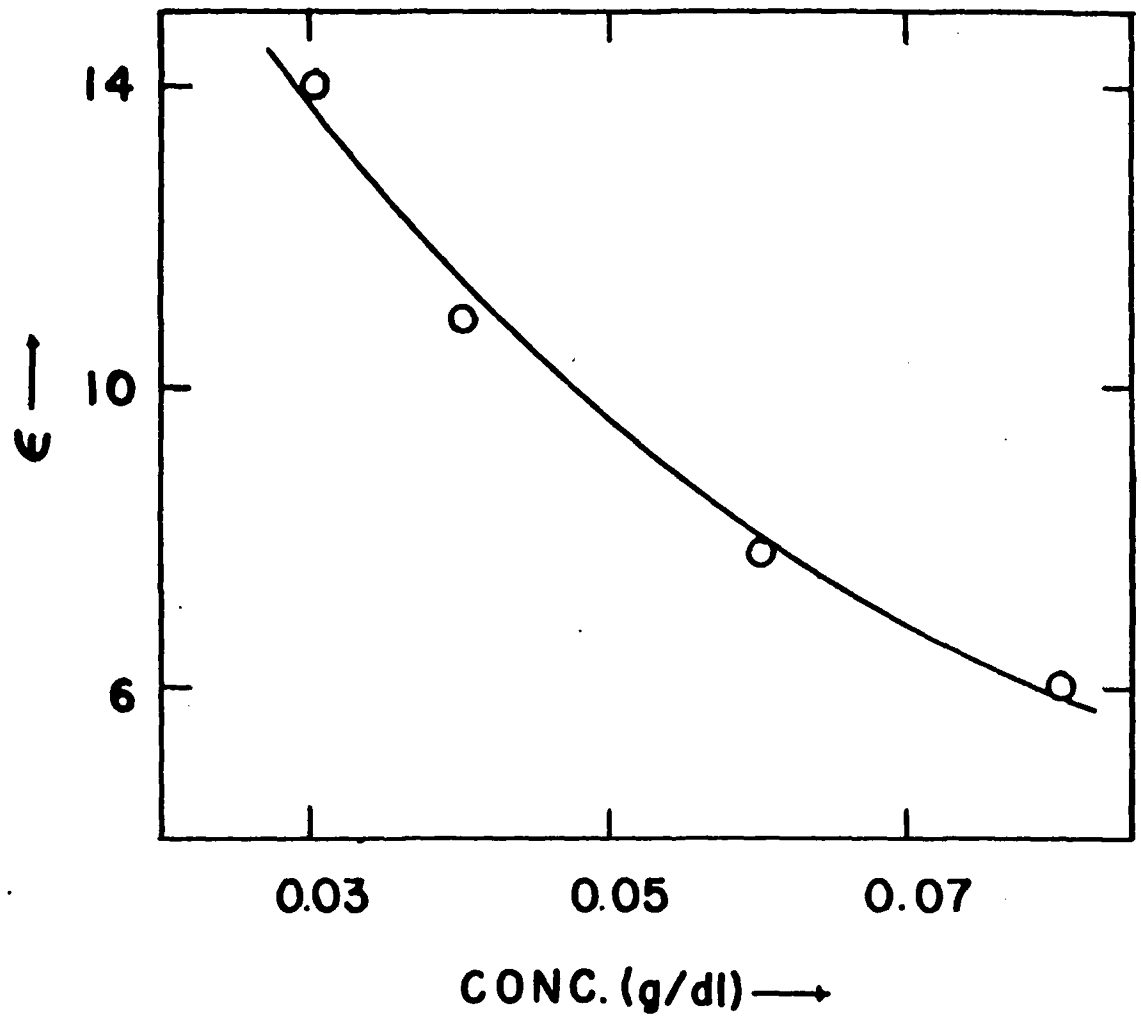

Figure 3 . Extinction coefficient versus concentration for solutions of PBFP in acetone.

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